



# The effect of $\text{Ca}^{2+}$ and $\text{Al}^{3+}$ additions on the stability of potassium disilicate glass as a soot oxidation catalyst

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## ABSTRACT

Potassium disilicate ( $\text{K}_2\text{Si}_2\text{O}_5$ ) glasses substituted with additions of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  have been prepared, characterized and tested as diesel soot oxidation catalysts. Ca and Al modify the silicate glass network, resulting in improved stability for catalyzing oxidation of diesel soot. TGA and water immersion studies showed that substituting  $\text{K}_2\text{O}$  with  $\text{CaO}$  can improve the chemical stability with a small loss of catalytic activity.  $(\text{K}_2\text{O})_{0.5}(\text{CaO})_{0.5}(\text{SiO}_2)_2$  had a soot ignition temperature ( $T_{ig}$ ) around  $410^\circ\text{C}$  and also excellent catalytic stability with repeated soot oxidation cycling. Similarly, substituting with  $\text{Al}^{3+}$  gave improved stability, with  $(\text{K}_2\text{O})_{0.7}(\text{Al}_2\text{O}_3)_{0.3}(\text{SiO}_2)_2$  exhibiting a  $T_{ig}$  around  $370^\circ\text{C}$  and better stability than  $\text{K}_2\text{O}\text{-}\text{Si}_2\text{O}_5$ . The activity results are interpreted with insights gained from FTIR characterization.

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## 1. Introduction

The high activity of potassium-containing catalysts for soot oxidation has attracted much attention over the past decade. Unfortunately, potassium containing catalysts usually tend to degrade after repeated thermal cycles due to the loss of potassium [1,2]. This is especially the case for  $\text{K}_2\text{CO}_3$  or  $\text{KNO}_3$ . This deactivation is thought to occur due to loss of potassium through sublimation. Thus the challenge in using potassium and other alkali metal based catalysts is minimizing, if not eliminating, the loss of the potassium or alkali metal. One approach often used is to incorporate K into a more stable structure (e.g. perovskites).

In many cases attempts to stabilize K were pursued by impregnating potassium species into a support material. This approach has been common over the past decade, with examples such as potassium catalyzed soot oxidation supported by  $\text{TiO}_2$  [3,4],  $\text{ZrO}_2$  [5],  $\text{Al}_2\text{O}_3$  [6,7] and  $\text{SiO}_2$  [2,8]. Among these support materials,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  do not show any catalytic effect while  $\text{ZrO}_2$  and  $\text{TiO}_2$  show very low activity in soot oxidation. The potassium– $\text{TiO}_2$  interaction and the improvement of contact conditions between soot and the catalyst, studied by means of thermal programmed reduction (TPR) and X-ray diffraction (XRD), were offered as an explanation for the activity differences for soot oxidation compared to catalysts

supported on alumina [6,7].  $\text{K}/\text{ZrO}_2$ , with a  $\text{K}/\text{Zr}$  ratio = 0.14, synthesized from potassium nitrates was reported as providing the highest activity. The reversible transformation of a bridged  $\text{NO}_3^-$  and a monodentate  $\text{NO}_3^-$  was suggested as a possible mechanism [5].

Studies on the application of K on silica supports were only recently reported [8,9]. Ogura et al. [8] tried to prevent potassium losses by using silica-alumina and zeolites as support materials and impregnating potassium as the active catalytic center. They found that the second test cycle of soot oxidation on K/sodalite showed higher activity than the first run. It appears that the state of potassium was changed under thermal conditions with a minor loss of the crystal structure of sodalite resulting from interaction of Al sites and K in aluminosilicate. However, no extended stability test was performed to reveal the longer-term catalytic performance in this study. Relatively extended stability testing was performed by López-Suárez et al. [2] when they studied the effect of copper on potassium stability in  $\text{K/SrTiO}_3$  catalyzed soot oxidation. According to their 6-cycle repeated TPR results, significant degradation was found between the first and second TPR cycle for all potassium catalysts. Even though the less active  $\text{Cu/SrTiO}_3$  catalysts do not degrade, the addition of copper into  $\text{K/SrTiO}_3$  structure does not affect the potassium stability.

Research has shown that catalysts with potassium can lead to high activity for soot combustion. Nevertheless, such catalysts can be readily degraded due to the loss of active potassium. Conversely, investigations showed that catalysts with immobile K ions that are rigidly bound in the lattice give lower activity and higher soot oxidation temperatures [10,11]. Neither case is ideally suited for the application on DPFs.

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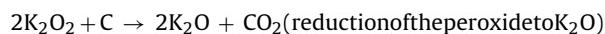
As an alternative one can consider the use of potassium containing glasses as catalysts [12]. This approach relies on the slow passive release of potassium from a silicate glass network to provide for renewal of the catalytic surface activity of the glass. The purpose is to mitigate the effect of loss of the active potassium species by providing new ions over time.

A diesel exhaust environment typically contains 5–7% water vapor at temperatures of 250–600 °C. For a catalytic glass introduced into this environment there are several possible degradation mechanisms that might affect the activity, including volatilization of K<sup>+</sup>, hydrothermal degradation of the glass, and surface alterations due to temperature excursions above the softening temperature of the glass,  $T_S$ . At the same time, vapor phase hydration of the glass is expected to occur in this ambient, with an ion exchange process promoting K<sup>+</sup> ion diffusion to the catalyst surface, where potassium hydroxide and carbonate can form. An imbalance between the rate of removal and resupply of the mobile K<sup>+</sup> ions could leave a K depleted layer and diminished activity. An overall schematic of the processes suggested to be occurring at the glass catalyst surface is shown in the sequence in Fig. 1.

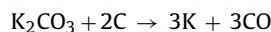
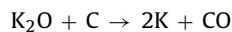
Beginning with a pristine surface (Fig. 1a) water vapor in contact with a silicate glass containing alkali oxides can cause ion exchange at the glass surface [14]. Alkali ions in the glass exchange with hydrogen ions and come to the surface (Fig. 1b), where potassium hydroxide subsequently develops by K<sup>+</sup> + OH<sup>-</sup> → KOH (Fig. 1c). The potassium hydroxide on the glass surface is rapidly converted to potassium carbonate by reaction with atmospheric carbon dioxide as 2KOH + CO<sub>2</sub> → K<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O (Fig. 1d).

From coal gasification studies it is known that a chemical interaction between potassium salts and carbon leads to formation of catalytically active species. Several alkali metal species have been proposed to be responsible for carbon gasification, including carbonate, oxidic and metallic species and a surface C-O-K phenolate complex. In several studies, the presence of mobile liquid particles was detected, suggesting the formation of a molten peroxide phase during the catalyzed oxidation reaction [15]. Peroxide formation was suggested to occur through the reaction K<sub>2</sub>CO<sub>3</sub> + C + O<sub>2</sub> → K<sub>2</sub>O + 2CO<sub>2</sub> (Fig. 1e) [15,16]. This reaction can provide a secondary carbon oxidation pathway. On the carbon surface the formation of C-O-K phenolate groups has also been observed [17,18]. The alkali metal ion facilitates the chemisorption of H<sub>2</sub>O and CO<sub>2</sub> on a bridge carbon atom, leading to the observed catalytic activity by the C-O-K group [19]. Decomposition of the carbonate to the peroxide [15] leads to the phenomenon of catalytic channeling (Fig. 1f), where the catalyst “drills” into carbon, as observed in several studies of graphite doped with alkali-metal carbonates [20–22]. Such mobility can enhance oxidation of soot under loose contact conditions, as occurs in a DPF. This could promote catalyst loss, but recent studies suggest that K ion loss is reduced when K<sub>2</sub>CO<sub>3</sub> is favorably bonded on a support, such as a perovskite [23].

Hence, the primary catalytic reaction is thought to occur through the oxidation-reduction cycle (Fig. 1f) [15,20]:

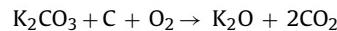
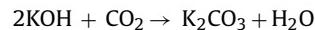
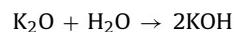


The fact that vaporization of the alkali metal is often reported in gasification studies, suggests the possibility of the reactions,



leading to sublimation (and subsequent loss) of the reduced metal [24]. However, these reactions typically only proceed at elevated temperatures (700–800 °C) and reduced pO<sub>2</sub> [16,20,24]. O<sub>2</sub>

involvement in the reaction scheme (i.e. that it is not due to steam or CO<sub>2</sub> gasification of the carbon soot) is suggested by the oxygen pressure dependence of the soot ignition temperature [12]. On a catalytic glass surface in a diesel exhaust environment possible additional reactions involve potassium oxide reacting with water vapor to form KOH, leading to the formation of K<sub>2</sub>CO<sub>3</sub> from KOH.



This may lead to reincorporation of K<sub>2</sub>O from a combusted soot particle onto the glass surface as K<sub>2</sub>CO<sub>3</sub>, thereby mitigating potassium loss.

The slow release of ions from the near-surface shaded potassium exchange region in Fig. 8 that is desired in a catalytic glass is the opposite of what is wanted for a durable, weather resistant glass. Several approaches to modeling glass durability have been described, primarily for predicting the durability of glasses for nuclear waste storage [25,26]. In that application, the goal is to minimize leaching from, or corrosion of, the glass, with researchers hoping to predict glass behavior over thousands of years. The approaches usually involve considering a glass as a mixture of species with known free energies of hydration. Glass durability is then predicted based upon thermodynamic hydration equations, with the contribution of the various species scaling with mole percentage of components present in the glass.

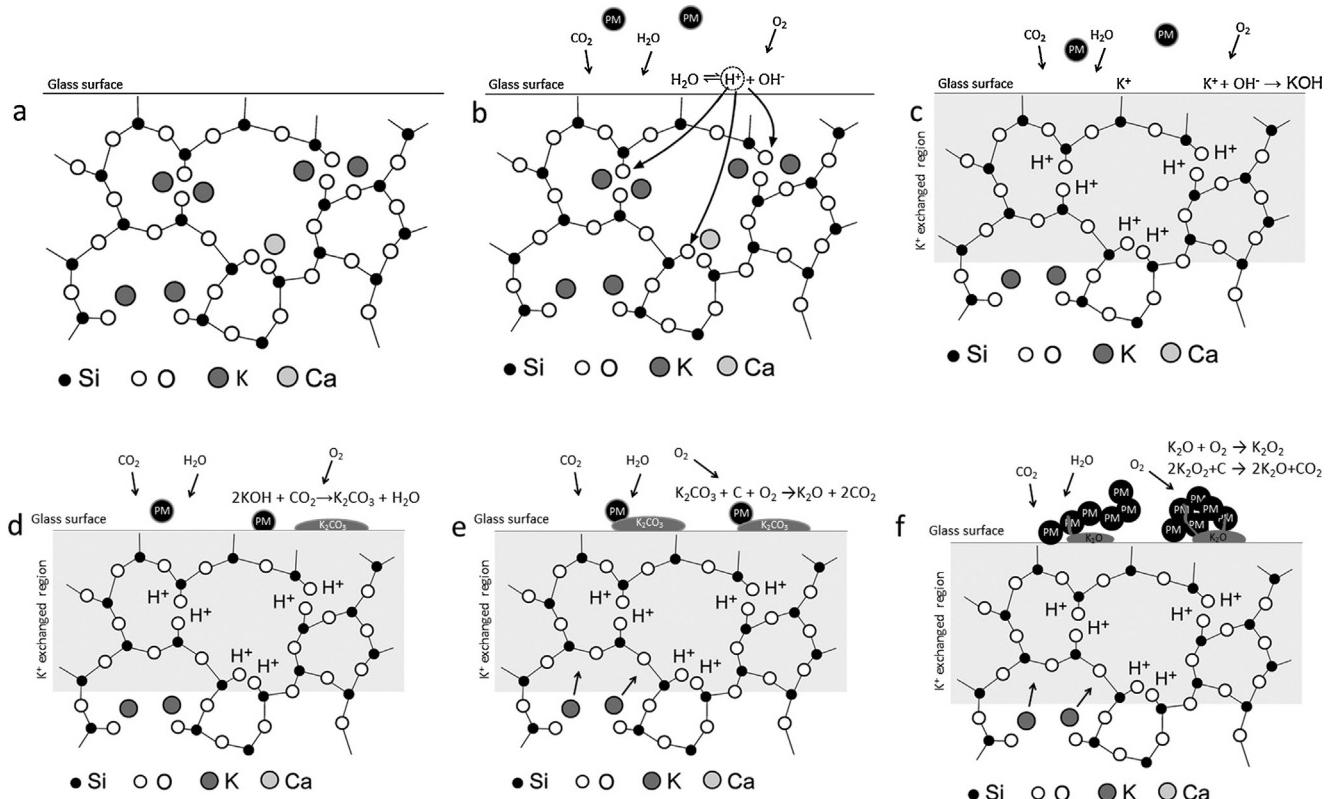
To design durable glasses, glass reactant species are selected depending on hydration reactions that are expected to occur between the glass and an aqueous solution (acidic or basic). This is based on expectations as to whether cations in the glass will anionically complex with silica or other oxides, which is determined from their relative anionic force, which denotes their field strength. The field strengths are considered along with the relative partial molar free energies of the hydration reactions ( $\Delta G_i$ ) of the cation species that can occur in an aqueous environment [27,28]. Essentially, a glass with poor weathering characteristics, as is desired for DPF application should incorporate relatively high levels of low field strength, highly negative free energy of hydration ion species (i.e. alkali ions).

For the novel application of glasses as soot combustion catalysts it is necessary to balance two characteristics of the glass: melting point and ion delivery. Not only is easy ion exchange desired, but the glass should have a melting point high enough to withstand the diesel exhaust environment without substantial softening or particle coarsening. During soot combustion, it is possible that local temperatures can reach 700–800 °C for brief periods. Thus a desirable glass possesses a relatively high melting point as well as facile ion exchange.

To investigate compositional effects in a catalytic glass, a good starting point is provided by the alkali disilicates (or “phylosilicates”), of the type M<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, where M is one or more alkali metal ions. The alkali disilicates are of particular interest because while some of them are very susceptible to degradation by moisture (e.g. K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) others are unaffected (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>). Potassium disilicate glass can provide a starting point for examining mixed ion effects in soot oxidation catalysts based on glass. In the present study we examine if such mixed ion effects can be observed in terms of soot oxidation activity.

## 2. Experimental methods

Potassium disilicate glass of composition K<sub>2</sub>O-2SiO<sub>2</sub>, Ca-doped potassium disilicates of composition (CaO)<sub>x</sub>(K<sub>2</sub>O)<sub>(1-x)</sub>(SiO<sub>2</sub>)<sub>2</sub>



**Fig. 1.** Sequence of the suggested soot combustion process by a glass catalyst starting with (a) a clean catalyst (K–Ca–Si–O) surface. (b) Exposure to water vapor in diesel exhaust leads to ion exchange, bringing K<sup>+</sup> to the surface. (c) Exchanged potassium ions at the surface react to form KOH while a near surface K depleted region slowly develops in the glass. (d) Further reaction of the KOH with CO<sub>2</sub> leads to formation of K<sub>2</sub>CO<sub>3</sub>. (e) K<sub>2</sub>CO<sub>3</sub> reacts with carbon to form K<sub>2</sub>O; K ions diffuse into depleted region. (f) K<sub>2</sub>O tunnels into surface soot deposits, catalyzing soot combustion, with CO<sub>2</sub> being evolved and K potentially being lost.

Adapted from [13].

( $x=0.1, 0.3, 0.5, 0.7, 0.9, 1$ ), and Al-doped potassium disilicates of composition ( $\text{Al}_2\text{O}_3$ )<sub>( $x$ )</sub>( $\text{K}_2\text{O}$ )<sub>1-x</sub>( $\text{SiO}_2$ ) <sub>$x$</sub>  ( $x=0.1, 0.3, 0.5, 0.7, 0.8, 0.9, 1$ ) were prepared using standard reagent grade  $\text{K}_2\text{CO}_3$  (99%),  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$  and quartz (99.9%  $\text{SiO}_2$ ) by a solid state synthesis method as described elsewhere [12]. Briefly, the precursors were mixed for 30 min in a SPEX Mill (SPEX Mixer/Mill 8000) with zirconia jar and balls and moved to  $\text{Al}_2\text{O}_3$  crucibles. The mixture was then heated up to 1100–1500 °C at 10 °C/min and held for 2 h before cooling down slowly to room temperature in the furnace. The obtained glass was ground into a powder with the SPEX Mill in a zirconia jar with zirconia balls for 30 min, and sieved to ~20 µm for further use.

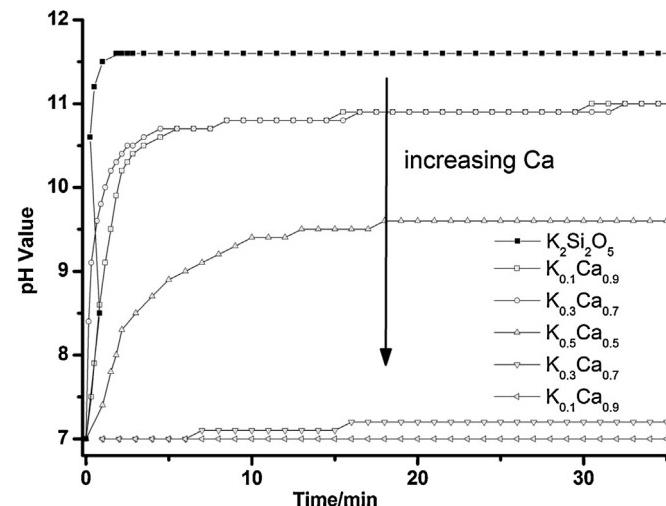
The synthesized silicate glass sample structures were analyzed using FTIR before and after repeated stability test cycles. For the FTIR measurement, an attenuated total reflectance (ATR) method was used (Biorad).

The softening temperatures of the silicate glass samples were measured with a Linseis L75 dilatometer. Briefly, the powder samples were pressed into pellets and heated in Ar in the dilatometer under a small load introduced by a push rod. The softening temperature ( $T_S$ ) is defined as the temperature where the sample reaches a maximum length during heating [29].

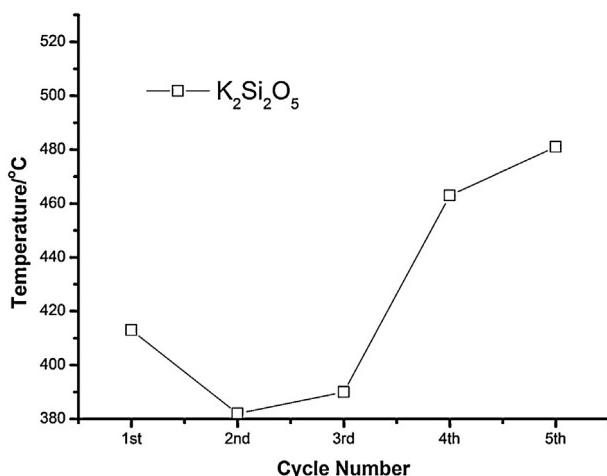
Immersion testing was performed to determine the ease of leaching surface potassium by water. The silicate glass powders were immersed in 100 ml of distilled water at 25 °C for different periods (1–3 h). The pH was measured periodically to assess the level of K<sup>+</sup> ion dissolution. Polypropylene containers were used to avoid any reactions between the electrolyte and container walls.

Soot oxidation was characterized by TGA (TA Instruments model 2950). Commercially available Printex-U carbon black (Degussa), with a specific surface area of 110 m<sup>2</sup>/g and apparent density of

370 kg/m<sup>3</sup>, was used as model soot in order to obtain reproducible and comparable results. A wet-deposition method described elsewhere [11] was used to mix soot with catalyst powders. Briefly, 50 µl of a carbon black/methanol suspension (1 g/10 ml) was mixed with 50 mg of catalyst for each sample to get an equivalent 10:1 weight ratio of catalyst/soot. Typically, approximately 0.5 mg of soot is combusted in each run with 5.0 mg of catalyst (10:1 catalyst/soot ratio). This is low enough soot mass to avoid thermal runaway concerns. A pre-mixed gas with a composition to



**Fig. 2.** Variation of the pH of the electrolyte with immersion time for K–Ca–Si–O catalyst powders.



**Fig. 3.** The change of  $T_{ig}$  for  $K_2Si_2O_5$  catalyzed soot oxidation with repeated TGA cycling.

simulate diesel exhaust (10%O<sub>2</sub>–5%CO<sub>2</sub>–%N<sub>2</sub>) was bubbled through water bottle to achieve about 3% water vapor in the feeding gas. The heating rate was 20 °C/min, which automatically decreased to ~2 °C/min when a transition was detected for improved resolution. The TGA balance and furnace gas flows were 80 and 120 ml/min, respectively.

Performance was evaluated based on the ignition temperatures ( $T_{ig}$ ) and when half of the soot was combusted ( $T_{50}$ ).  $T_{ig}$  was determined from the extrapolated onset temperature for the weight loss corresponding to carbon oxidation. This is the temperature at the intersection of the extrapolated baseline prior to decomposition and the tangent to the weight loss transition line in the TGA curve. The catalytic activity of the glass relies on the presence of K ions at or near the surface. Some fraction of the near surface K can be lost during carbon combustion [11]. In order to examine the stability of the catalysts on soot oxidation, the same compounds were subject to repeated soot application and combustion studies in the TGA up to 5 cycles.

### 3. Results

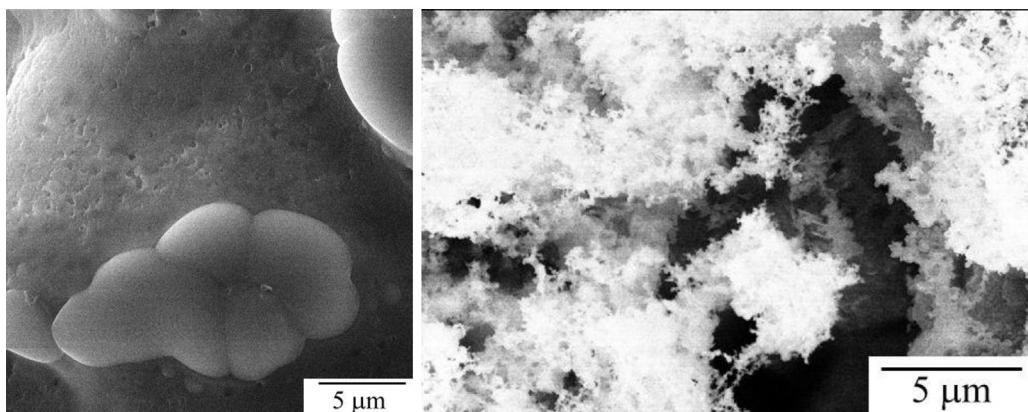
Ca and Al additions are known to affect the extent of interaction of silicate glasses with water. Fig. 2 shows the variation of pH during the water immersion test of K–Ca–Si–O catalysts. The pH value increased to saturation at a much faster rate with  $K_2Si_2O_5$  immersion compared with any of the doped compounds. The pH changes are due to leaching of K<sup>+</sup> from the glass surface region through

ion-exchange reactions between –Si–O–K bonds and protons in the aqueous ambient. As the level of CaO (or Al<sub>2</sub>O<sub>3</sub>, tested but not shown) substitution increased, the rate of pH increase slowed. The decrease of pH for K–Ca–Si–O silicate immersion with the increase of Ca<sup>2+</sup>/Al<sup>3+</sup> doping reflects an increase of chemical durability that prevents water/silicate interactions. Since the soot oxidation by K containing catalysts relies on the “active potassium” [11], a large decrease of surface K concentration or too much of an increase of K stability could lead to a decrease of catalytic activity and reactivity. The dependence of catalytic activity on glass stability is seen in some of the soot combustion tests described below.

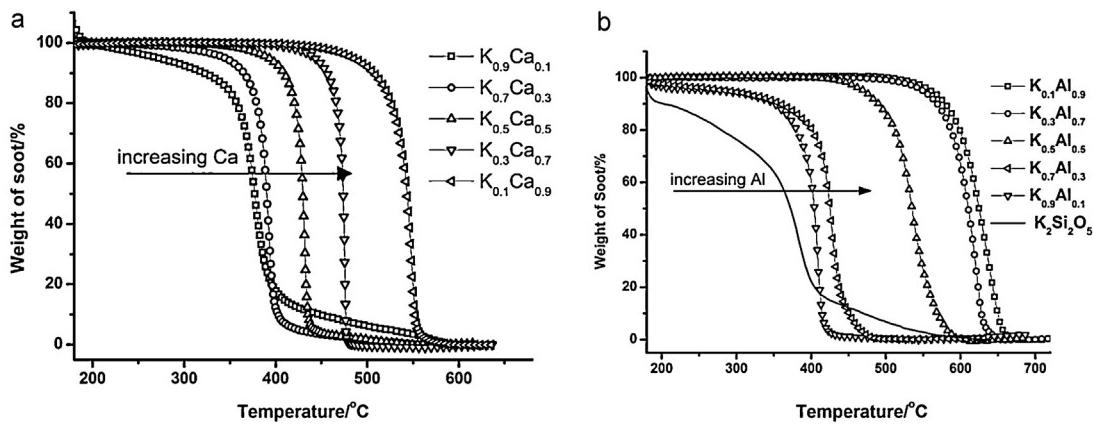
Fig. 3 shows the  $T_{ig}$  of  $K_2Si_2O_5$ -catalyzed soot oxidation as function of multiple soot combustion cycles. The initial  $T_{ig}$  is 410 °C, and is lower (380 °C, 390 °C) in the second and third cycles, but further TGA cycling showed that the  $T_{ig}$  increased to 485 °C after 5 cycles. Such a change is not unexpected, given the hygroscopic nature of  $K_2Si_2O_5$ . For example, morphological changes are easily observed in films of  $K_2Si_2O_5$ . When  $K_2Si_2O_5$  was applied to an inert substrate by sol–gel processing [30], a change was observed as a result of soot oxidation. Fig. 4 shows a  $K_2Si_2O_5$  surface before and after 3 cycles of soot oxidation. The white fluffy phase is a SiO<sub>2</sub>-rich compound based on XRD and FTIR study. This shows that  $K_2Si_2O_5$  catalyst is not stable during soot oxidation. This type of decay with cycling has been seen in other K-containing compounds [2,10,11].

Substitutions of Ca and Al can have an effect on the soot oxidation behavior as seen in Fig. 5. Fig. 5a shows the catalytic soot oxidation curves of  $(CaO)_x(K_2O)_{(1-x)}(SiO_2)_2$  ( $x=0.1$ –0.9) ternary silicates, which are denoted as  $Ca_{0.1}K_{0.9}$ ,  $Ca_{0.3}K_{0.7}$ , etc.  $Ca_{0.1}K_{0.9}$  catalyzed soot oxidation at the lowest  $T_{ig}$ , and the soot oxidation temperature increased continuously with the increase of Ca doping. It was observed that  $Ca_{0.1}K_{0.9}$  was very hygroscopic, tending to absorb moisture even in the ambient atmosphere. The weight loss below 350 °C can be attributed to the loss of absorbed moisture from the silicate. This was confirmed by cycling a sample in the TGA without exposure to moisture. When reheated the 2nd time the baseline is flat like the higher Ca content samples. Only the weight loss above 350 °C is used in soot conversion calculations. When Ca<sup>2+</sup> doping is greater than 0.3, the hygroscopicity decreases dramatically, with minimal weight loss observed below the soot oxidation temperature.

Fig. 5b shows the catalytic soot oxidation curves of  $(Al_2O_3)_x(K_2O)_{(1-x)}(SiO_2)_2$  ( $x=0$ –0.9) ternary silicates, which are denoted as  $Al_{0.1}K_{0.9}$ ,  $Al_{0.3}K_{0.7}$ , etc. A trend similar to Ca<sup>2+</sup> doping was also found for Al<sup>3+</sup> substitution, where  $T_{ig}$  increased with an increase of Al<sup>3+</sup> content. The  $T_{ig}$  increased very little when the Al<sub>2</sub>O<sub>3</sub> substitution increased from 0.1 to 0.3, but increased significantly between 0.3 and 0.5.  $Al_{0.5}K_{0.5}$  showed moderate activity with  $T_{ig}$  of ~480 °C, while  $Al_{0.7}K_{0.3}$  and  $Al_{0.9}K_{0.1}$  barely



**Fig. 4.** The SEM images of  $K_2Si_2O_5$  coating (a) before and (b) after 3-cycle soot oxidation testing.

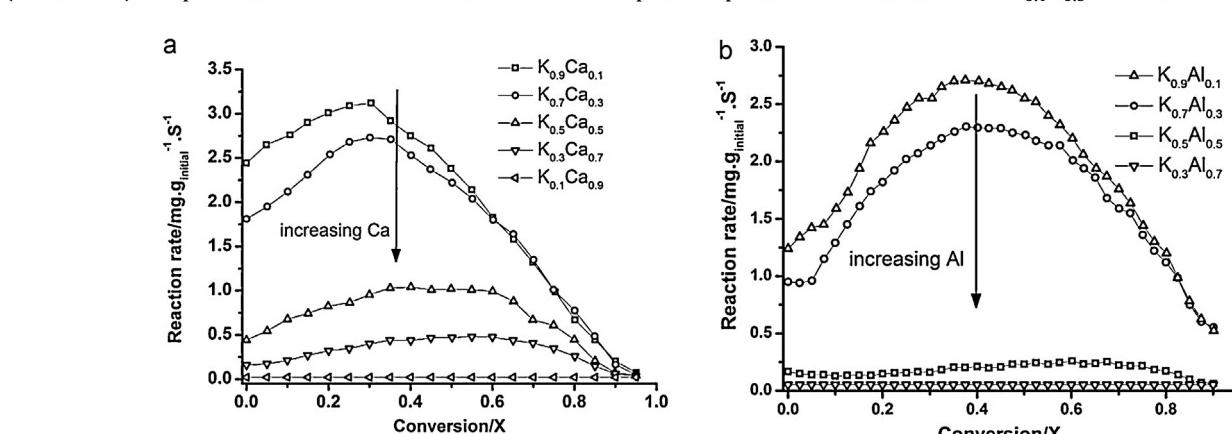


**Fig. 5.** (a) TGA curves for soot oxidation by  $(\text{CaO})_x(\text{K}_2\text{O})_{(1-x)}(\text{SiO}_2)_2$ , for  $x=0.1, 0.3, 0.5, 0.7, 0.9$ ; (b) TGA curves for soot oxidation by  $(\text{Al}_2\text{O}_3)_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_2$ , for  $x=0.1, 0.3, 0.5, 0.7, 0.9$ . Feed: simulated diesel exhaust (10%  $\text{O}_2$ –5%  $\text{CO}_2$ –3%  $\text{H}_2\text{O}$ – $\text{N}_2$ ).

showed any activity for soot oxidation. Although addition of  $\text{Al}^{3+}$  was observed to decrease the hygroscopicity of  $\text{K}_2\text{Si}_2\text{O}_5$ , the K-Al-Si-O compounds are still hygroscopic until  $\text{Al}^{3+}$  doping is greater than 0.5.

Isothermal testing of catalytic soot oxidation by compounds in the  $(\text{CaO})_x(\text{K}_2\text{O})_{(1-x)}(\text{SiO}_2)_2$  and  $(\text{Al}_2\text{O}_3)_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_2$  ternary silicate systems was carried out at 380 °C in a simulated exhaust gas environment. The samples were heated to 380 °C under inert gas flow ( $\text{N}_2$ ). The gas flow was then switched to the reaction gas at time zero. The reactivity (units of  $\text{mg/g}_{\text{initial}}^{-1} \text{s}^{-1}$ ) was calculated from the derivative of soot oxidation conversion with time ( $r = dX/dt$ ), where  $X = \text{fraction converted mass } ((m_0 - m_t)/m_0)$ , with  $m_0$  being the initial weight of soot, and  $m_t$  the remaining mass of soot at time  $t$ . Fig. 6 shows the change of reactivity vs. conversion with  $\text{Ca}^{2+}$  doping (Fig. 6a) and with Al doping (Fig. 6b).

The reactivity of K-Ca-Si-O silicates for catalyzing soot oxidation showed an obvious decrease with the introduction of  $\text{Ca}^{2+}$ , and a significant activity drop can be seen when  $\text{Ca}^{2+}$  increased from 0.3 to 0.5. An increase of  $\text{Al}^{3+}$  doping also resulted in a decrease in the reactivity, with the reactivity dropping dramatically when  $\text{Al}^{3+}$  doping increased from 0.3 to 0.5. It was found that equivalent amounts of  $\text{Al}^{3+}$  usually produced lower reactivities than  $\text{Ca}^{2+}$  doping. For instance,  $\text{Ca}_{0.3}\text{K}_{0.7}$  showed an activity maximum of  $2.7 \text{ mg g}_{\text{initial}}^{-1} \text{s}^{-1}$ , compared with  $2.2 \text{ mg g}_{\text{initial}}^{-1} \text{s}^{-1}$  for  $\text{Al}_{0.3}\text{K}_{0.7}$ . While  $\text{Ca}_{0.7}\text{K}_{0.3}$  and  $\text{Ca}_{0.5}\text{K}_{0.5}$  both showed modest activity (maxima of  $0.5 \text{ mg g}_{\text{initial}}^{-1} \text{s}^{-1}$  and  $1.05 \text{ mg g}_{\text{initial}}^{-1} \text{s}^{-1}$  respectively) their Al-substituted counterparts of  $\text{Al}_{0.7}\text{K}_{0.3}$  and  $\text{Al}_{0.5}\text{K}_{0.5}$  barely showed any activity. No reactivity was observed for the  $\text{K}_{0.1}\text{Ca}_{0.9}$  or  $\text{K}_{0.1}\text{Al}_{0.9}$  (not shown) compounds. The maximum observed in the samples



**Fig. 6.** Soot oxidation reactivities for (a)  $(\text{CaO})_x(\text{K}_2\text{O})_{(1-x)}(\text{SiO}_2)_2$ , for  $x=0.1, 0.3, 0.5, 0.7, 0.9$ ; (b)  $(\text{Al}_2\text{O}_3)_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_2$  for  $x=0.3, 0.5, 0.7, 0.9$ . Feed: simulated diesel exhaust (10%  $\text{O}_2$ –5%  $\text{CO}_2$ –3%  $\text{H}_2\text{O}$ – $\text{N}_2$ ).

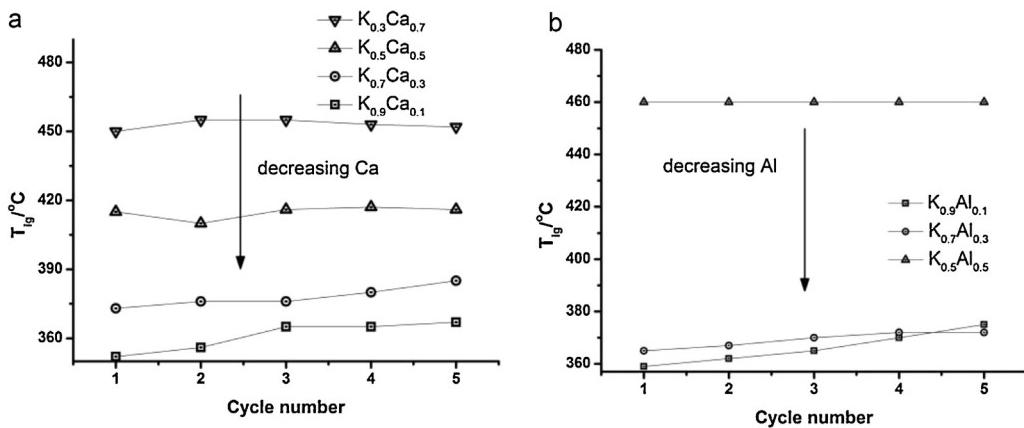
**Table 1**

$T_{50}$  Temperature variation with repeated TGA combustion cycling for  $(\text{CaO})_{2x}(\text{K}_2\text{O})_{(1-x)}(\text{SiO}_2)_2$  and  $(\text{Al}_2\text{O}_3)_x(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_2$ .

Cycle	K/Ca ratio				K/Al ratio		
	0.9/0.1	0.7/0.3	0.5/0.5	0.3/0.7	0.9/0.1	0.7/0.3	0.5/0.5
1	379	386	428	470	395	420	522
2	377	390	430	473	400	421	522
3	380	390	433	470	403	423	522
4	385	401	430	473	407	421	522
5	390	403	431	472	408	422	522

with higher reactivity may reflect a change in the nature of the soot-catalyst contact as oxidation proceeds [31].

Repeated TGA experiments were performed for both  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  doped potassium silicates to determine the catalytic stability of the compounds during soot oxidation. The results for  $\text{Ca}^{2+}$ - and  $\text{Al}^{3+}$ -doped potassium disilicates are presented in Fig. 7a and b respectively. The change in  $T_{ig}$  is shown in Fig. 7, but the  $T_{50}$  values show similar trends, as seen in Table 1. No degradation in soot oxidation catalytic activity (as gauged by  $T_{ig}$ ) was found for  $\text{Ca}_{0.9}\text{K}_{0.1}$ ,  $\text{Al}_{0.9}\text{K}_{0.1}$  and  $\text{Al}_{0.7}\text{K}_{0.3}$ , but the activities of these compositions are comparatively small, with high ignition temperatures. It can be seen that all the doped samples showed improved catalytic stability compared to  $\text{K}_2\text{Si}_2\text{O}_5$  (shown in Fig. 3), which quickly degraded. The  $T_{ig}$  and  $T_{50}$  for  $\text{Ca}_{0.1}\text{K}_{0.9}$ ,  $\text{Ca}_{0.3}\text{K}_{0.7}$  increased slightly after 5 combustion cycles, while no degradation was found for  $\text{Ca}_{0.5}\text{K}_{0.5}$  and  $\text{Ca}_{0.7}\text{K}_{0.3}$  catalysts. Similar trends can be observed for  $\text{Al}^{3+}$  doped potassium silicates, where  $\text{Al}_{0.1}\text{K}_{0.9}$  showed obvious degradation,

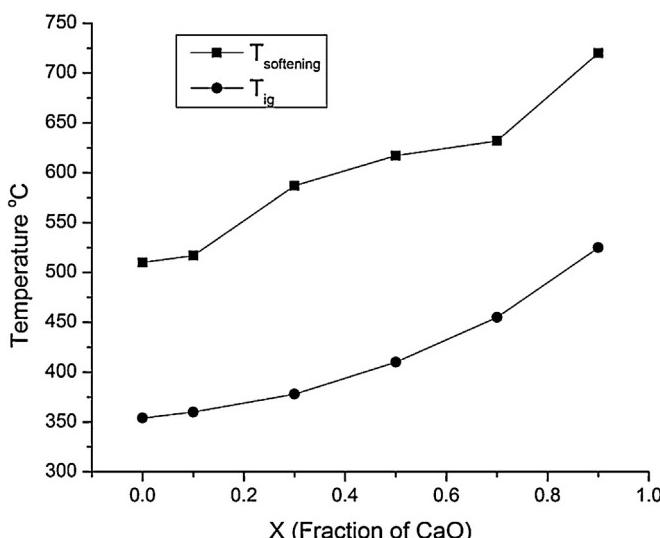


**Fig. 7.** Soot oxidation  $T_{ig}$  variation with repeated TGA combustion cycling for (a):  $(CaO)_x(K_2O)_{(1-x)}(SiO_2)_2$ , for  $x=0.1, 0.3, 0.5, 0.7$ ; and (b)  $(Al_2O_3)_x(K_2O)_{(1-x)}(SiO_2)_2$  for  $x=0.1, 0.3, 0.5$ .

with  $T_{ig}/T_{50}$  increasing by 15 °C after 5 combustion cycles, while  $Al_{0.3}K_{0.7}$  only showed slight degradation with ~5 °C increase in the  $T_{ig}$  and  $T_{50}$  values.

The glass softening temperature ( $T_S$ ) also reflects the relative network strength, and is an important characteristic of a potential DPF glass catalyst, since local exhaust temperatures might exceed  $T_S$ , possibly affecting the activity. Additions that improve the corrosion resistance of a glass (i.e. less  $K^+$  ion exchange) also typically increase  $T_S$ , as seen in Fig. 8 which shows the trends in  $T_S$  and  $T_{ig}$  of  $(CaO)_x(K_2O)_{(1-x)}(SiO_2)_2$  ternary silicates with increasing Ca substitution.

A continuous increase of  $T_{ig}$  and  $T_S$  was found for the K-Ca-Si-O silicate system with an approximate difference between  $T_{ig}$  and  $T_S$  of 200–250 °C. In our studies  $Al_2O_3$  had a similar effect, but the  $T_S$  exhibited a more abrupt increase from 640 °C to 900 °C when the  $Al_2O_3$  fraction ( $x$ ) increased from 0.5 to 0.7. The temperature difference between  $T_S$  and  $T_{ig}$  in the K-Al-Si-O system has a broader distribution ranging from 200 to 350 °C, with the smallest difference occurring at a  $K^+ : Al^{3+}$  molar ratio of 1. If  $T_S$  is too low, a silicate glass catalyst may flow too readily at expected DPF temperatures, resulting in blocking of the filter micropores. The Ca and Al substitutions that increase  $T_S$  can also degrade the catalytic activity. Clearly a balance needs to be struck between these two counter trends.



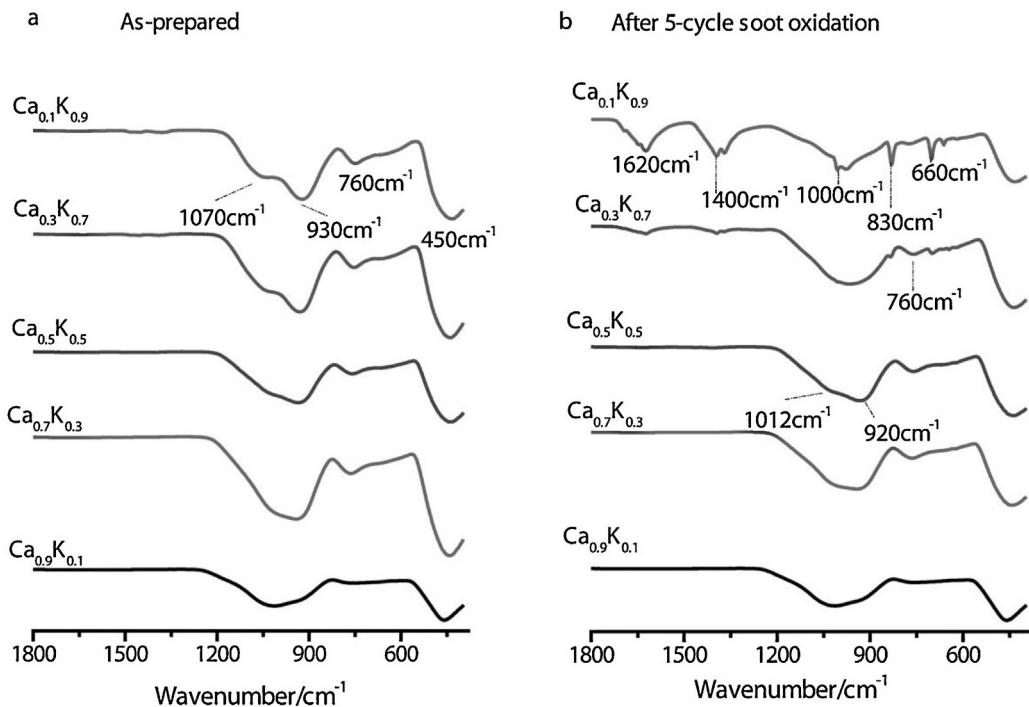
**Fig. 8.** (a)  $T_S$  and  $T_{ig}$  of  $(CaO)_x(K_2O)_{(1-x)}(SiO_2)_2$  as a function of CaO composition for  $x=0.1, 0.3, 0.5, 0.7, 0.9$ .

The infrared spectra of the K-Ca-Si-O and K-Al-Si-O silicate powders from 400 to 1700 cm<sup>-1</sup> before and after 5 soot oxidation cycles are shown in Figs. 9 and 10, respectively. The IR spectrum of potassium disilicate showed absorption bands including one at 450 cm<sup>-1</sup> from Si-O-Si rocking, one at 760 cm<sup>-1</sup> indicative of Si-O-Si bending, a band at 930 cm<sup>-1</sup> from Si-OH stretching and bands at 1070 and 1220 cm<sup>-1</sup> from asymmetric Si-O-Si stretching [32,33]. As can be seen in Fig. 9a, the IR spectra as a function of  $Ca^{2+}$  doping do not change dramatically except for the obvious shift and diminishing of the Si-OH 930 cm<sup>-1</sup> band with an increase of  $Ca^{2+}$  concentration. Fig. 9b shows the IR spectra of the K-Ca-Si-O silicate catalysts after 5 soot oxidation cycles. In comparison with the corresponding as-prepared silicates, significant changes can be seen for  $K_{0.9}Ca_{0.1}$  and  $K_{0.7}Ca_{0.3}$  catalysts after repeated soot oxidation cycles. The absorption bands at 830 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> can be assigned to carbonate (expected from the formation of  $K_2CO_3$ ), and the 1620 cm<sup>-1</sup> band is from  $\delta$ -OH bending vibration of physically adsorbed water. No change can be seen when  $Ca^{2+}$  doping ( $x$ ) is greater than 0.5.

When  $Al^{3+}$  was introduced ( $x=0.1–0.3$ ), the 760 cm<sup>-1</sup> band shifted toward lower frequencies (Fig. 10a), while the shift of the 1020 cm<sup>-1</sup> band to higher frequencies can be attributed to  $Al^{3+}$  induced changes in Si-O-Si bond angles [32]. Obvious shifting and diminishing of 930 cm<sup>-1</sup> of the Si-OH band with an increase of  $Al^{3+}$  concentration can also be seen. In comparing the spectra of the potassium disilicates with higher  $Al^{3+}$  doping, it is seen that when  $x \geq 0.5$ , the spectra of  $Al^{3+}$  doped potassium silicates showed three main bands at 445, 587, 638 cm<sup>-1</sup> related to Al-O vibration [33–35], while the 930 cm<sup>-1</sup> silanol groups (Si-O-H) can barely be seen. Relative to the spectra of the as-prepared silicates, the spectra of K-Al-Si-O compositions after soot oxidation (Fig. 10b) showed changes only in the low  $Al^{3+}$  doped samples ( $K_{0.9}Al_{0.1}$  and  $K_{0.7}Al_{0.3}$ ), with the presence of new bands of carbonate at 830 and 1400 cm<sup>-1</sup>, as well as the 1620 cm<sup>-1</sup> band from adsorbed water. No change can be observed for samples with higher  $Al^{3+}$  doping levels ( $x \geq 0.5$ ).

#### 4. Discussion

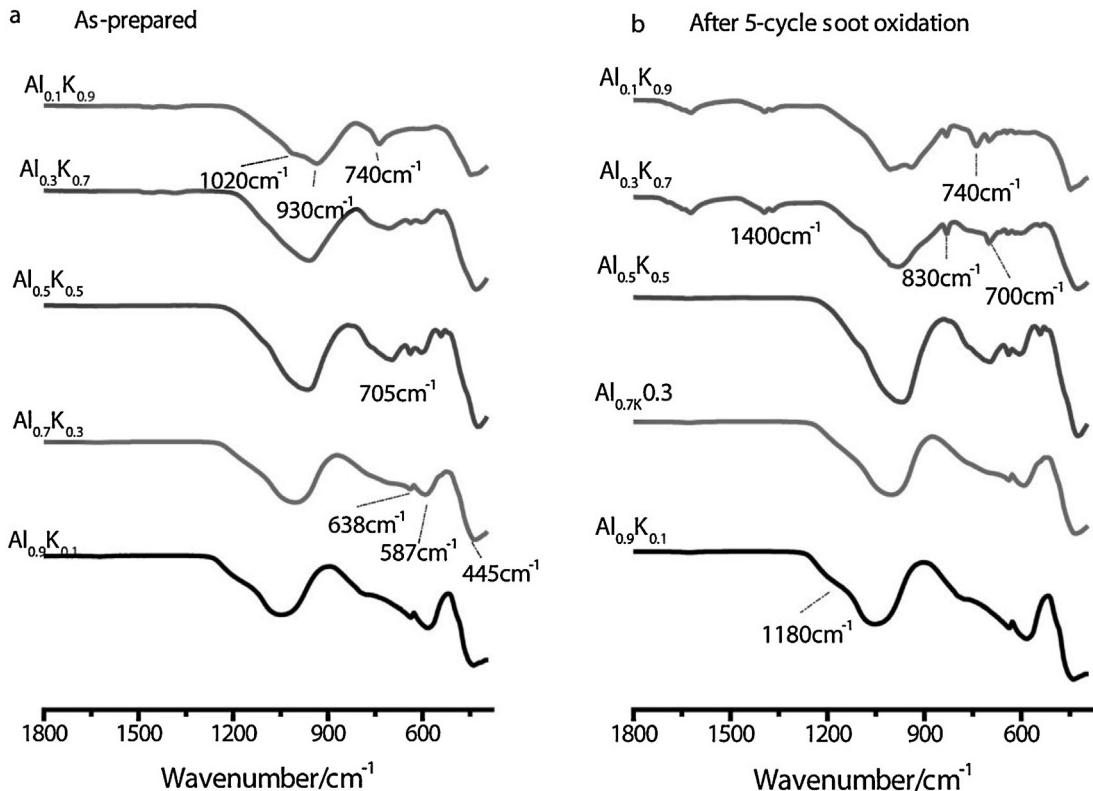
Unlike chemically stable silica with a highly ordered silicon-oxygen tetrahedral structure, potassium disilicate is much less stable due to the formation of non-bridging oxygen (NBO), which decreases the connectivity of the Si-O-Si tetrahedra. Each NBO must be associated with nearby potassium to maintain local charge neutrality (see Fig. 1). The K ions occupy the interstices in the network, reducing the unoccupied free volume of the structure. As the K content is increased, the concentration of NBO



**Fig. 9.** FTIR spectra of the K-Ca-Si-O silicate system: (a) as-prepared powders; (b) after 5 soot oxidation cycles. Wave numbers at  $450\text{ cm}^{-1}$  are from Si–O–Si bending, at  $760\text{ cm}^{-1}$  are indicative of Si–O–Si stretching, a band at  $930\text{ cm}^{-1}$  from Si–OH stretching, and bands at  $1070$  and  $1220\text{ cm}^{-1}$  are from asymmetric Si–O–Si stretching.

increases and the concentration of bridging oxygen (BO) decreases, directly in proportion to the potassium oxide content, until a network can no longer be maintained. Hence increasing K destabilizes silica.

A tetrahedron fully linked into the network via four BO is designated as a  $Q_4$  unit, while an isolated tetrahedron with no BO is designated as  $Q_0$  unit [29]. It is assumed that only  $Q_3$  units will be produced until every tetrahedron in the network is linked by



**Fig. 10.** FTIR spectra of the K-Al-Si-O silicate system: (a) as-prepared powders; (b) after 5 soot oxidation cycles. The absorption bands at  $830\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  can be assigned to carbonate, and the  $1620\text{ cm}^{-1}$  band is from  $\delta$ -OH bending vibration of physically adsorbed water.

three BOs and one NBO. For a general glass compositional formula:  $x\text{K}_2\text{O}\cdot(100-x)\text{SiO}_2$ ,  $Q_4 = 100 - 3x$  and  $Q_3 = 2x$ . The average number of NBO per tetrahedron can be written as [29]:

$$\frac{\text{NBO}}{\text{Tetrahedron}} = \frac{2x(1)}{x(1) + (100-x)(2)} = \frac{2x}{100-x}$$

Hence, for the composition of potassium disilicate ( $\text{K}_2\text{O}\cdot2\text{SiO}_2$ ), only  $Q_3$  exists in the glass network and there is an average of one NBO in each  $Q_4$  tetrahedron.

For the simple K–Ca–Si–O silicate system  $x(\text{K}_2\text{O})\cdot y(\text{CaO})\cdot(100-x-y)\text{SiO}_2$ , the concentration of  $Q_n$  species can be calculated in a manner analogous to  $x\text{K}_2\text{O}\cdot(100-x)\text{SiO}_2$  by replacing  $x$  with  $(x+y)$ . Since the molar ratio of  $\text{SiO}_2$  was fixed at 66.7% in this study and the only substitution was replacing  $\text{K}_2\text{O}$  with  $\text{CaO}$ , the  $(\text{CaO})_x(\text{K}_2\text{O})_{(1-x)}(\text{SiO}_2)_2$  system is supposed to be  $Q_3$  unit dominant as well. When  $\text{Ca}^{2+}$  is introduced, each  $\text{Ca}^{2+}$  must have two neighboring NBO, so  $\text{Ca}^{2+}$  additions provide stronger network linkages at the alkali earth sites. Additionally, the replacement of a more mobile monovalent alkali ion by the less mobile divalent alkali earth ion reduces the net mobility of the modifier ion through the network, and therefore, improves the chemical durability [36].

The above discussion on the structural function of  $\text{Ca}^{2+}$  doping in potassium disilicate also explains the increase of  $T_S$  associated with the increase of  $\text{Ca}^{2+}$  doping and the increase in durability during immersion testing. The decrease of pH value for K–Ca–Si–O silicate immersion with an increase of  $\text{Ca}^{2+}$  doping reflects an increase of chemical durability that can prevent water/silicate interactions from taking place. Since soot oxidation by K containing catalysts relies on the availability of “active potassium” [11], a decrease of surface K concentration or an increase of K stability can lead to a decrease of catalytic activity and reactivity. If K is lost from the surface during repeated soot oxidation, it will be less easily replaced in more stable glasses. In the catalytic activity test (Fig. 5) the  $\text{Ca}_{0.3}\text{K}_{0.7}$  composition showed a rather low soot oxidation temperature of 380 °C and degraded slightly after 5 repeated cycles (Fig. 7). The soot oxidation temperature of the  $\text{Ca}_{0.5}\text{K}_{0.5}$  composition increased to around 410 °C, but no  $T_{ig}$  degradation was found for this compound. The infrared spectrum of post-reaction  $\text{Ca}_{0.5}\text{K}_{0.5}$  did not show any peak from carbonate or adsorbed water after soot oxidation. The sum of these results suggest that the optimized molar ratio of  $\text{Ca}^{2+}$  should between 0.3 and 0.5 ( $x=0.3-0.5$ ) for  $(\text{CaO})_x(\text{K}_2\text{O})_{(1-x)}(\text{SiO}_2)_2$  ternary silicates.

It is generally assumed that most of the aluminum in potassium silicate glasses will reside in aluminum–oxygen tetrahedra, so long as the total concentration of alkali oxides equals or exceeds that of alumina. These tetrahedra substitute directly into the network for Si–O tetrahedra. Since Al–O tetrahedra with 4 bridging oxygens have an excess negative charge of –1, an associated cation must be present in the vicinity of each such tetrahedron to maintain local charge neutrality. One might then visualize the aluminum–oxygen tetrahedron as a large anion with an effective –1 charge distributed over the entire anion. The associated modifier cation can be located anywhere in the immediate vicinity of this anion [29].

The distinct absorption bands of Al–O tetrahedra in the  $\text{Al}_{0.5}\text{K}_{0.5}$  IR spectrum imply that there is a significant change in the structure compared to  $\text{Al}_{0.7}\text{K}_{0.3}$ . Since the oxygen supplied by the  $\text{K}_2\text{O}$  component is consumed in the formation of the Al–O tetrahedra, it is not available for the formation of NBO. In other words, each added  $\text{Al}^{3+}$  can be considered to remove one NBO from the silicate structure. When the total concentration of  $\text{K}^+$  exactly equals that of  $\text{Al}^{3+}$ , the structure is supposed to be a fully linked network of  $Q_4$  units, where the cation in any specific  $Q_4$  unit can be either silicon or aluminum, with no NBO present.

This structural model for alkali aluminosilicate can explain the abrupt change of glass properties (e.g.  $T_S$  and IR spectra) for the  $(\text{Al}_2\text{O}_3)_{(x)}(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_2$  ternary silicates when  $x$  decreased to 0.5. The activity of  $\text{Ca}_{0.3}\text{K}_{0.7}$  and  $\text{Al}_{0.3}\text{K}_{0.7}$  compounds are equivalent with  $T_{ig}$  of ~380 °C, and both are subjected to degradation after extensive soot oxidation experiments. Nevertheless, in comparison with the increase (by 30 °C) of  $T_{ig}$  for  $\text{Ca}_{0.5}\text{K}_{0.5}$ , the  $T_{ig}$  of  $\text{Al}_{0.5}\text{K}_{0.5}$  compound increased by 80–460 °C. Even though  $\text{Al}_{0.5}\text{K}_{0.5}$  did not show any degradation after the 5-cycle soot oxidation experiment, the high soot oxidation temperature implies this compound is too stable to serve as an effective soot oxidation catalyst. Thus, the optimized molar ratio of  $\text{Al}^{3+}$  should between 0.3 and 0.5 ( $x=0.3-0.5$ ) for  $(\text{Al}_2\text{O}_3)_{(x)}(\text{K}_2\text{O})_{1-x}(\text{SiO}_2)_2$  ternary silicates.

Several explanations for the role played by potassium in soot combustion reactions in conventional oxides (e.g. transitional metal oxides) have been proposed, including that: (1) K can increase the amount of chemisorbed oxygen on a perovskite surface [37]; (2) K promotes the formation of eutectic compounds [38]; (3) K promotes carbon consumption to form carbonate intermediates [39]; (4) K acts as an electron donor to enhance the reactivity of metal–oxygen bonds [40]. It has been suggested that in the case of potassium oxide or carbonate in an  $\text{O}_2$  rich atmosphere, carbon oxidation is facilitated by formation and reduction of potassium peroxide ( $\text{K}_2\text{O}_2$ ) [20]. Decomposition of potassium carbonate to the peroxide [16] can lead to the phenomenon of catalytic channeling, where the catalyst “drills” into carbon, as observed in several studies of graphite doped with alkali-metal carbonates [20–22]. This “active” potassium is not tightly bound in a lattice, so may be lost during long term operation at relatively high temperature, causing loss of catalytic activity [11].

Soot oxidation tests performed on potassium disilicate ( $\text{K}_2\text{O}\cdot2\text{Si}_2\text{O}_5$ ) glass showed significant degradation after repeated cycles. As noted above, the loss of K can be brought about by through an ion exchange mechanism. Alkali ions, i.e. potassium and sodium are examples of network modifiers that have low field strengths and therefore high mobility, so in silica they will lead to a glass that will permit relatively easy ion exchange, allowing easy removal of cations from the near-surface region of the glass.

The replacement of the more mobile monovalent alkali ion by a less mobile divalent alkali earth ion  $\text{Ca}^{2+}$  (or  $\text{Al}^{3+}$ ) will reduce the net mobility of  $\text{K}^+$  ions through the network, and result in improved chemical durability as seen in Fig. 2. By taking advantage of the ion-exchange process in amorphous silicates, the slow release of potassium ions from a silicate glass can act as a source of potassium to compensate for surface K loss, prolonging the lifetime/stability of a catalyst. Fig. 6 shows that there is also an effect of Ca and Al substitutions for K on the catalytic soot oxidation curves of ternary silicates.  $\text{Ca}_{0.1}\text{K}_{0.9}$  catalyzed soot oxidation at the lowest  $T_{ig}$ , and the soot oxidation temperature increased continuously with the increase of Ca (or Al) substitution. However, too high of additions of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  resulted in glass that were overly stable, and thus exhibited decreasing activity for soot oxidation with repeated cycling.

The glass softening temperature is also linked to the glass network structure. As seen in these results, an increase in thermal stability came at the expense of reduced catalytic activity. The  $T_S$  of catalysts applied to a DPF needs to be reasonably high. If the softening temperature is too low (along with the viscosity), the silicate glass catalyst might easily flow at expected DPF temperatures, possibly blocking the monolith micropores. On the other hand, if the softening temperature is too high, at moderate DPF temperatures replenishment of surface K lost during soot oxidation may be severely limited. Considering the temperatures inside a diesel exhaust system can occasionally reach 600–700 °C, the  $T_S$  of the silicate catalysts should appropriately be at least higher than 600 °C.

Hence, further modifications to some of the compositions examined here might be desired (e.g. varying SiO<sub>2</sub>) in order to increase the softening temperature.

While potassium containing glasses offer promise as potential soot oxidation catalysts for diesel particulate filter applications, further studies are needed to determine the effect of other possible species such as NO<sub>x</sub> and SO<sub>x</sub>. For example, if exposure leads to the formation of KNO<sub>3</sub> or K<sub>2</sub>SO<sub>4</sub>, this could tie up K and reduce activity. However, one study shows K<sub>2</sub>SO<sub>4</sub> can convert to K<sub>2</sub>CO<sub>3</sub> and carbon oxidation can continue [41]. Characterization of surfaces after long term exposure to a diesel environment is needed to identify the extent of formation of K-containing surface phases (e.g. K<sub>2</sub>O, K<sub>2</sub>CO<sub>3</sub>), and to determine if K is lost in the combustion process, or tied up in non-reactive phases.

## 5. Conclusions

Potassium disilicate (K<sub>2</sub>O·2Si<sub>2</sub>O<sub>5</sub>) glass substituted with different CaO/K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O ratios were synthesized, characterized and tested for soot oxidation by TGA in simulated exhaust gas. It was found that substituting K<sub>2</sub>O with CaO gives a glass with improved chemical stability, but this also sacrifices the catalytic activity. Ca<sub>0.1</sub>K<sub>0.9</sub> and Ca<sub>0.3</sub>K<sub>0.7</sub> compounds showed high activities, but *T*<sub>ig</sub> and *T*<sub>50</sub> degradation was observed with repeated soot combustion cycling. Ca<sub>0.5</sub>K<sub>0.5</sub> showed somewhat less catalytic activity (*T*<sub>ig</sub> ~410 °C) but also significantly improved catalytic stability. Similarly, doping Al<sup>3+</sup> in (Al<sub>2</sub>O<sub>3</sub>)<sub>(x)</sub>(K<sub>2</sub>O)<sub>1-x</sub>(SiO<sub>2</sub>)<sub>2</sub> between *x* = 0.3–0.5 gave good soot oxidation activity and improved stability compared to K<sub>2</sub>O·2Si<sub>2</sub>O<sub>5</sub>.

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